Cr12362

UNITED STATES ATOMIC ENERGY COMMISSION

ISC-108

THE POLAROGRAPHIC DETERMINATION
OF SMALL AMOUNTS OF CHROMIUM IN CALCIUM
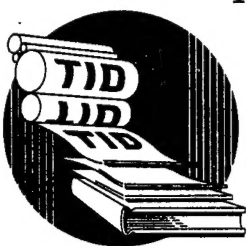
By
Doris V. Stage
Charles V. Banks

April 24, 1950

Iowa State College

Technical Information Division, ORE, Oak Ridge, Tennessee

19970306 075

The Polarographic Determination of Small Amounts of Chromium in Calcium*

by Doris V. Stage and Charles V. Banks

When a need arose for the determination of small amounts of chromium in calcium metal, a rapid, direct method involving no separations was naturally desired. Thus, two methods, colorimetric and polarographic, were suggested. Of the two, a polarographic method seemed the more promising.

Demassieux and Heyrovsky (1), Spálenka (2), Prajzler (3), and Kolthoff and Lingane (4) have reported that chromium is reduced stepwise at the dropping mercury electrode giving two well-defined waves. The half-wave potentials are given as-0.88 volt and-1.53 volts vs. the saturated calomel electrode (S.C.E.) in 0.1 N potassium chloride (4). The first wave corresponds to the reduction of chromic ion to chromous ion, and the second to the reduction of chromous ion to the metal. With acid solutions of the chromic ion only the first wave is observable before the hydrogen wave.

Prajzler (3) made use of both chromium waves in a simultaneous determination of iron, chromium, and aluminum. Spálenka (2) also used both waves to determine zinc and chromium simultaneously. Lingane and Pecsok (5) report that the diffusion current of the first wave is directly proportional to the total salt concentration.

It seems, then, that the polarographic determination of chromium should be a simple, rapid method. However, most of the workers used chromium concentrations of the order of 10^{-3}M, while concentrations used in this work are of the order of 10^{-5}M. Also, the concentration of the supporting electrolyte used was usually 0.1M or less. Although this is the optimum concentration generally (5), a higher concentration of the supporting electrolyte, a calcium salt, must be used here in order that the chromium concentration may be high enough to be determined directly. Nevertheless, it was found that, under the proper conditions, the diffusion current of the first reduction of chromic ion is proportional to the concentration. Thus, a fairly rapid method of determining or at least of estimating, the concentration of small amounts of chromium present in calcium metal is provided.

Urone, Druschel, and Anders (6) describe a very sensitive method for the polarographic determination of chromium in dusts and mists. These authors oxidize the chromium compounds to chromate and run them polarographically in a 1N sodium hydroxide solution. Unfortunately,

this method cannot be applied to calcium metal without prior separation of chromium because of the very low solubility of calcium hydroxide.

Apparatus

A Sargent Model XXI recording polarograph was used for this work. The cells used were H-type cells with a side arm for flushing the sample with nitrogen. Contact between the saturated calomel half-cell and the solution was made through a saturated potassium chloride-agar bridge. In a few cases a cell with an asbestos fiber bridge was used. The dropping mercury electrode was that supplied with the instrument. The supplementary damping provided on the instrument was used in all determinations to facilitate measurement of the diffusion currents. The temperature was kept at $25^\circ \pm 0.1^\circ$ by a constant temperature water bath. A Beckman Model M pH meter was used for most of the pH measurements.

Reagents

Ammonium hydroxide, reagent grade.
Anhydrous calcium chloride, reagent grade. Many lots of calcium chloride contain small amounts of chromium which are extremely difficult to remove. Some very pure calcium chloride which gave no chromium wave when run polarographically at the highest sensitivity was obtained and used in these experiments. A 2 M stock solution was prepared.

Chromic chloride, reagent grade. A 0.01 M stock solution was prepared.
    the solution was standardized by fuming with sulfuric acid,
    oxidizing to chromate with excess ammonium peroxydisulfate and
    a small amount of silver nitrate, and titrating with ferrous
    sulfate and ceric sulfate. The solution was diluted to 0.001
    M for use.
Hydrochloric acid, reagent grade.
Sodium sulfite, reagent grade. A 0.1 M solution was prepared and diluted to 0.01 M for use.
Sulfanilic acid, C. P. grade.

Experimental Work

Since calcium may be dissolved by conversion to calcium chloride fairly readily, the latter was chosen as the supporting electrolyte.

One molar calcium chloride was found to be the optimum concentration.
If the concentration is much higher, the chromium wave is somewhat
suppressed while in a much lower concentration of calcium the con-
centration of chromium present in solution is too low to be polaro-
graphically determined. The half-wave potential of the first chromium
wave in this medium is about -1.0 volt vs. S.C.E. although it varies
somewhat with the amount of chromium present. Solutions using calcium
perchlorate gave essentially the same results.

It is suggested in the literature (4),(5) that a small amount of
gelatin be used as a maximum suppressor in the determination of chro-
mium. However, in this case gelatin suppresses the chromium wave.
This is in agreement with the literature (4),(7) which states that
gelatin above a certain concentration, has a suppressive effect upon
the diffusion current and that calcium ion has a suppressive effect
upon negative maxima. Thus, probably the high concentration of cal-
cium completely suppresses any maximum that might occur, and addition
of even a very small amount of gelatin suppresses the wave itself.

It was found that the length of time that nitrogen is flushed
through the solution is quite important. A flushing time of 35 minutes
at a moderate rate (2 to 3 bubbles per second) was found to be neces-
sary to insure elimination of oxygen and reproducibility of the wave.

Lingane and Pecsok (5) report that 3.8 is the optimum pH for the
chromium wave. It was found that this is true in these determinations
and that polarograms are quite sensitive to pH in this range. While
somewhat lower pH values can probably be used, a nearly constant pH
is required. Values of 3.7 ± 0.1 are recommended. A small amount
of sulfanilic acid may be added to act as a buffer. Although several
reagents were considered in an attempt to find a suitable buffer for
this solution, sulfanilic acid was the only one tried which did not
interfere with the chromium wave.

In some calcium samples ferric iron is present to such an extent
that it forms a troublesome precipitate. Kolthoff and Lingane (4)
report that ferric ion can be reduced by hydroxylamine hydrochloride
in the polarographic determination of chromium. It was found that this
reagent interferes with the determination of chromium when 1M calcium
chloride is used as the supporting electrolyte. Sodium sulfite, how-
ever, is satisfactory for the reduction of iron in this procedure,
since the sulfite is reduced at a more positive potential (-0.5 volt
vs. S.C.E.) than is the chromium and small amounts do not affect the
chromium wave.

The chromium waves obtained were not entirely satisfactory, since
they were not as well-defined as one might like. This is believed to

be due to a combination of factors, such as the low concentration of chromic ion (of the order of $10^{-5}M$), the high sensitivity used (0.003μa/mm. for most of the work), and the irreversibility of the reaction (5),(8). Best results were obtained if the step height was between 20 mm. and 75 mm. By altering the sensitivity, waves lying within this range can usually be obtained, except for the lowest concentrations of chromium.

Results given in Table I were obtained using an unbuffered solution of chromium-free calcium chloride to which known amounts of chromium were added. The concentrations are given in parts of chromium per million parts of calcium. A few results obtained from solutions buffered with sulfanilic acid were almost identical with those obtained from the unbuffered solutions.

Recommended Procedure

A 4.0 g. sample of calcium is treated (Cautiously) with enough water to convert all the metal to the hydroxide which is then dissolved in a minimum amount of concentrated hydrochloric acid. The solution is diluted to 50 or 60 ml. and 0.2 g sulfanilic acid is added. When the sulfanilic acid has dissolved, the pH is adjusted to 3.7 $\pm$ 0.1 with ammonium hydroxide, using a dilute solution (1:10) to make the final adjustment. The solution is diluted to 100 ml. in a volumetric flask. About 10 ml. of the solution is placed in the cell and flushed 35 minutes with nitrogen to remove dissolved oxygen. The amount of chromium present is best determined from a calibration curve although the standard addition method may be used (9).

Table I

Polarographic Determination of Chromium in Calcium

Chromium Taken, p.p.m.	Diffusion Current, mm.[a]	Chromium Found, p.p.m.	Error, p.p.m.
9	< 4	< 10	—
13	4	10	-3
26	12	31	+5
39	15	39	±0
52	16	43	-9
52[b]	19	50	-2
65	22	58	-7
104	38	100	-4
104[b]	43	112	+8
130	50	130	±0
156[b]	60	156	±0
195	73	190	-5
260	105	273	+13

[a] Sensitivity, 0.003μa/mm.

[b] Sulfanilic acid added.

Summary

A polarographic method for the determination of small amounts of chromium in calcium metal is proposed. The diffusion current of the first chromium wave, occurring at -1.0 volt vs. the saturated calomel electrode in 1M calcium chloride, was found to be directly proportional to the concentration. Factors affecting the diffusion current are discussed, and optimum conditions for the determination are described.

Literature Cited

(1)   M. Demassieux and J. Heyrovsky, J. chim. phys., 26 (1929) 219.

(2)   M. Spálenka, Metallwirtschaft, 23 (1944) 346.

(3)   J. Prajzler, Collection Czechoslov. Chem. Communs, 3 (1931) 409.

(4)   I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience
      Publishers, Inc., New York, N. Y., 1946.

(5)   J. J. Lingane and R. L. Pecsok, J. Am. Chem. Soc., 71 (1949) 425.

(6)   P. F. Urone, M. L. Druschel, and H. K. Anders, Anal. Chem., 22
      (1950) 472.

(7)   I. M. Kolthoff and J. J. Lingane, Chem. Rev., 24 (1939) 1.

(8)   R. L. Pecsok and J. J. Lingane, J. Am. Chem. Soc., 72 (1950) 189.

(9)   J. K. Taylor, Anal. Chem., 19 (1947) 368.

END OF DOCUMENT